

USE OF NEARINFRARED SPECTROSCOPY TECHNOLOGY FOR ASSESSMENT OF THE INTERNAL QUALITY OF SOME FRUITS AND VEGETABLES. REVIEW

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ABSTRACT

The purpose of this review is to classify the received NIRS results on assessment of the internal quality of some fruits and vegetables (particularly apples, peaches and potatoes) on the following criteria: Products; Quality index; Informative wavelength(λ - nm); Measurement mode and Literature source.

Keywords: nearinfrared spectroscopy, assessment of the internal quality, fruits and vegetables

Abbreviations: near infrared (NIR); nearinfrared spectroscopy(NIRS); soluble solids content (SSC); alcohol insoluble solids (AIS); reflectance (R); transmittance (T); visual spectral regions (VIS), standard error of prediction (SEC (P)); multiple correlation coefficient (RSQ); partial least-squares (PLS) ; principal component regression (PCR); standard error of cross-validation (SECV); standard normal variable (SNV); dry matter content (DM).

Introduction

The success of fruit and vegetables commercialization is to a great extent depending on their attractive appearance for the final consumer or processor (1). The size of a fruit or vegetable and the intensity of its basic and secondary coloration are the attributes most frequently taken into account by the consumers in making their purchasing decision. These quality features are included in the operative standards (or regulation documents) for fresh fruit and vegetables (2, 3, 4, 5). Although the consumers buy those products mainly relying on their appearance the next time purchase will be decided upon in dependence on the quality as perceived by eating. The most important objective indices of the internal quality and maturity degree of apples, peaches and potatoes are: soluble solids and sugars content, titratable acidity, sugars to acidity ratio. Under the conditions of up to date market economy the SSC has already been accepted as an index of considerable effect on the level of retail prices of fruits and vegetables (1, 6, 7). The integration of the internal quality parameters in the overall assessment of fruits and vegetables requires the implementation, in primary handling of those commodities, of new technologies for precise, non-destructive and quick on-line measurement of the above mentioned indices. With this respect real possibilities are offered by determination of soluble solids content (1, 8, 7, 9).

The optical properties of fruits and vegetables are important characteristics for the assessment of quality. Early developments concentrated on the use of visible light to determine ripeness. However, near infrared can provide information on the composition of produce, such as sugars and oils. Some of the earliest work in the field of NIR used near visible and visible radiation to provide information about fruit and vegetable quality.

In modern scientific and industrial practice NIR Spectroscopy is used for non-destructive determination of some indices of the internal quality, most frequently total and soluble solids content, starch, acidity, chlorophyll (in fruits and vegetables), protein (in grains), and total nitrogen content (in leaves). For fruits and vegetables, particularly, such kind of investigations have been

made on potatoes, onions, apples, peaches, other stone fruits, melons, oranges, mandarins, papaya and dates (1, 6).

Another line of NIR Spectroscopy applications is the detection of internal defects, e.g. fruit flesh browning. NIR methods in transmittance give greater possibilities for non-destructive determination of the internal color – that is of considerable importance for peaches.

There are numerous published work on non-destructive quality assessment of fruits and vegetables by means of spectroscopic methods in the VIS and near infrared NIR spectral regions. We shall mention some of these tracing the recent advances in optical methods.

During five years research Kalinov et al., (10) studied the shelf life potential of apples Red and Golden Delicious. These authors used a number of indices: starch index, fruit flesh firmness, electric impedance of fruit tissue; measurement of light transmittance and reflectance; total and soluble solids content, total sugar content, titratable acidity, mineral content (Ca, K, Mg, Na) as well as the emissions of CO₂ and ethylene. The results obtained have shown that only the optical indices and SSC are well correlated with the characteristic degree of maturity at harvest (within a 30 days harvesting period). In long term refrigerated storage the spectral transmittance changes but not in correlation with the basic processes determining the sensory quality of fruits, namely the texture softening and flavor changes. At the same time, however, the surface color of apples Golden Delicious remained well correlated with the quality of fruits.

Chalucova and Dimitrova (11) investigated the spectral characteristics of transmittance of some fruit and vegetables. She proposed systems for assessment of their maturity and also for tomato's maturity development during transportation and storage. The results are directed to realize systems for automatic sorting by color (12, 13). These studies later underwent future developments and they were directed basically toward the spectral characteristics of potatoes from the viewpoint of the recognition of external and internal defects (14, 15, 16, 17, 18). It has been achieved significant results also in the field of green pea's maturity assessment by measuring the transmittance in the NIR region (13). The recent achievements of the international research team that has been formed in order to create a new nondestructive technology for the "on-line" assessment of the internal quality of fruits and vegetables using NIR spectroscopy are expressed by numerous publications and presentations (13, 19, 20, 21), commented in that particular report in detail.

Apple texture calibrations have been recorded by Kwang Cho et al.,(22) using penetrometer readings as the reference method. Full range scanning equipment and an inexpensive filter instrument was used in this work.

The use of NIR has been used in the assessment of the maturity of vining peas (23). This work was undertaken at Campden and Chorleywood Food Research Association, UK together with partners of MIRELITE-Hungary, CANRI-Bulgaria and VTT-Finland. Calibrations were developed for pea firmness and AIS. Subsequent work was carried out on sweet corn which yielded good calibrations (24,25). The performance of these calibrations were highly dependent on information collected from the visible region of the spectrum.

Birth's(8) studies have shown that spectral methods can successfully be used for prediction of the total solids content in onions. It has been derived regression equation based on the transmittance at the wavelength $\lambda = 906$ nm, being in the vicinity of carbohydrates absorption band, with a correlation coefficient $r \geq 0.995$. The author believes that the method will be in principle applicable for non-destructive determination of protein, carbohydrates and lipids in fruits and derived products. NIR Spectroscopy in direct transmittance within the range 800 to 1000 nm has been used for determination of DM in sliced and whole potato tubers (26). Correlations obtained between the spectral data and reference chemical ones are: $r = 0,975$ for thin slices; $r = 0,952$ for thick slices and $r = 0,918$ for whole tubers. NIR calibrations have been developed for a range of properties of potatoes (27). The accuracy of this calibration was limited in comparison with compositional analysis of lower moisture foods.

NIR methods have also been used for the quantification of total carotenoids and sugars present in different carrot varieties (28) The authors found satisfactory results for the carotenoid calibration. The results of spectral measurements in transmittance (400-1000 nm) reported in (29) have proved the possibility of detecting internal defects in the main brown stalk of endive.

Peiris et al.,(30) have successfully determined soluble solids content in processing tomatoes.

NIR spectroscopy has also been used to determine the nutritive constituents in Chinese cabbage, rape and amaranth (31).

NIR has also been used for food safety reasons. Ito et al.,(4) have successfully employed a visible-near infrared spectroscopic system which offered potential for non-destructive nitrates determination in vegetables.

NIR based technology has also been used quite successfully to determine the ripeness of melons (3). A visible/near visible optic fibre probe was used to obtain spectra from 400-1100nm. The results from experimentation demonstrated that an NIR fibre-optic probe could be used to obtain measurements of melon ripeness to the required degree of accuracy, i.e +/-2.5 Brix. Herrera et al., (32) have used NIR spectrometry for estimation of ripeness in Chilean wine grapes. Samples were analysed for total soluble solids content. It was possible to estimate wine grape ripeness by using a portable spectrometer. It was found that there was greater accuracy for the red grape models, than the white grape models.

The feasibility of near infrared spectrometry, as a rapid and non-destructive alternative method for determining fruit maturity in avocado has been reported (33). Several batches of fruit were scanned individually in reflectance mode in the wavelength range of 1200 to 2400 nm. Dry matter content was measured for each fruit. NIR models showed good prediction accuracy for maturity.

Studies have also been employed on kiwi fruit, where NIR instruments have been used to establish harvesting dates and maturity changes in the field and cool store (Costa et al., 2000).

As to the studies of internal quality determination in fruit most attention was paid to apples.

Meurens et al.,(35) directed their research to detection of a number of internal defects: vitrescence, mealiness and internal discoloration (“brown core”) by spectroscopy in the visual and NIR regions. Compared to sound fruits the defective ones presented spectral features that were in correlation with the internal defects. The accuracy of diagnostics was always higher than 90% and near to 100% correct prediction. The spectra in absorption were measured within the range 550 to 1150 nm. The work of Herold et al.,(9) has shown that the spectrophotometric research on chlorophyll allows for determination of both harvest and consumption maturity as well as the detection of bruise injuries in Jonagold and Cox apples. The investigations were carried out in mode of absorption within the VIS/NIR regions. The spectral ranges 600 to 750 and 900 to 960 nm were accepted as informative for chlorophyll. Spectra were evaluated by the second derivatives. The achieved accuracy of classification by maturity was 98,3 % for Cox apples and 99,2% – for Jonagold. When pooled for the two varieties the percentage of correct classification was reduced to 98 %. It was still lower in prognostics – 85,8 %. Apples were correctly classified by bruising defects within the spectral range 600 to 750 nm in 94-95 % of the total number of fruits. McGlone et al.,(36) recorded visual and NIR spectra of Royal Gala apples within the range 500 to 1100 nm. The fruit samples were harvested during seven weeks from eight regions in two years replications, thus a wide range of maturity stages was covered. As quality indices were used: the basic color of the skin; firmness measured by a penetrometer; starch index (iodine test); SSC; starch content measured chemically, and titratable acidity. The predicting models obtained were judged as unreliable: $r = 0,5$ to $0,8$. Particularly interesting are the results obtained recently in the International Project ASTEQ (29, 37, 38, 39, 40, 41, 42, 43). Applying various methods and instruments the quality of Jonathan and Cox apples was determined. The appearance and internal quality were mainly accessed by spectrometry within the wavelength range 400 to 1700 nm. The

apples used were selected in three advancing degrees of maturity and one overripe. Good results have been obtained in determination of maturity degree. The detection of defects from bruising (at 1200 nm) has been evaluated as “promising”. It has been confirmed the possibility of detection and measurement of degree of mealiness and other kinds of internal defects. As a problem in these investigations (1, 7, 40) was indicated the difference in fruits coloration in the years of experimentation. To overcome that problem the research was focused on the NIR range from 1000 to 2500 nm.

Peirs et al.,(44) investigated apples of 7 varieties and 3 orchards in order to determine the harvest maturity. Fruit quality indices used were the same as in (36) with the addition of pH value and respiration rate. These indices were predicted by reflectance spectra with $r^2 = 0,89 - 0,93$. Very good and accurate determination of optimal harvest day (within 4 to 7 days period) were obtained by measurement of respiration rate minimum – $r^2 = 0,91 - 0,96$.

For the purpose of rapid grading a quick assessment of apples texture has been investigated by Moons et al., (45). A study for the assessment of changes in apple fruits over time has also included examining the texture of intact and peeled fruits. (46).

Laurens and Bertrand(47) carried out spectrophotometric measurements in absorption within the range 400 to 2000 nm with a gap of 2 nm on fruits of 6 apples varieties (Gala, Elton, Golden Delicious, Jonagold, Breaburn and Fuji) with the aim at possible classification by ripeness. The fruit samples were harvested on three successive dates with an interval of 1 month in three degrees of maturity defined as “pre-harvest”, “optimal” and “post harvest”. As informative were used the wavelengths 454, 537, 669 (chlorophyll) and 1925 nm. Out of altogether 300 measurements 260 gave correct classification by maturity degree. The varieties were well recognizable.

Studies in France (48) have indicated that NIR spectroscopy is an useful technique in order to be followed the apple fruits development on the tree, respectively the course of ripening process, and mostly – determination of harvest maturity. The studied cultivars comprised 4 table varieties (Elstar, Gala, Fuji, and Smoothee) and 2 cider apples (Douce Moen and Kermerien) taken from one region. For the first two early varieties of table apples was applied 5-stage scale to describe the physiological development, while for the remaining late varieties – a 6-stage scale was used. For spectroscopic measurements the range 1100 to 2198 nm was used with a gap of 2 nm and averaging of the spectra from the two halves of a fruit. The cultivars in the verification sets were in general well identified by discriminant analysis with 78 to 98,5 % correct identifications, and early varieties were clearly distinguished from the late ones.

The studies of Tongming et al.,(31) confirmed the great potential of NIR for determination of various sugars and vitamin C in intact strawberries and apples. The authors stated that the method could be applied in analyses of vegetables nutritive value as well as for evaluation of germplasm in plan breeding work. Considerable advance has been marked in the use of VIS/NIR Spectroscopy in industrial devices and machines for measurement of apple maturity and detection of bruises and internal defects (49).

Up to now in the USA it is not a practice apple fruits to be classified by internal defects but the fruit trade branch is looking for appropriate methods to this end (50). It is considered that firmness and sugar content are important indices of quality. A sensor and device working in NIR region in reflectance have been constructed. A prediction model for the above mentioned attributes has been developed and valuated with apples of the varieties Red Delicious, Golden Delicious and Empire. In (51) it has been reported about a similar device developed in France. It is used for spectrometric determination of sugar content, internal color (through it – maturity degree) and mechanical properties (maturity). Data about sugar determination are very good – error of validation 0,5% only.

Within the Project FAIR-CT97-3399,(52) it has been proposed a device for spectrometric determination of sugar, internal color (and by means of it – maturity degree) while

the mechanical properties are measured by a sound sensor .Tests were carried out on various varieties of nectarines and apples. Results can be used for development of classification system.

On-line internal quality sorting for apples has been commercially trialled in the US. The NIR system measured soluble solids in the fruit(53). It was tested at a packing plant of Stemilt Growers Inc., Wenatchee, Washington. Sorting based on SSC has been implemented in Japan with more than 60 sorting machines (6). The first ones were used for peaches and further on – for sorting of apples and other kinds of stone fruits. In result of 7 years efforts a prototype has been created of machine for determination of acidity in mandarins. The Mitsui Co. has defined an “index of maturity” based on the SSC and chlorophyll content values. Rather with such development, there has not yet applied classification into several quality groups depending on the measured characteristics. Initial positive results have been obtained in Italy for determination of apples and yellow flesh peaches maturity by spectrometric measurements within the range 400-1100 nm in partial transmittance mode as well as by means of a sensor device called “electronic nose” (1).

NIR models have been developed for soluble solids content in apples by means of reflectance spectra acquired within the range 380-2000 nm during 4 years of experimentation. The effect of the orchard was also studied in two climatic regions. The climatic condition was found to be of basic importance. For good prediction results a maximum number of samples in calibration set are needed.

Another, second by importance, object of NIR research on fruits is the peaches.

A non-destructive method has been developed for measurement of soluble solids content in peaches “Blake” by NIR Spectrometry (54) Transmittance was measured within the range 800 to 1050 nm in peaches of different degree of ripeness during three successive years. Multiple linear regression models have been derived using two wavelengths, second derivative spectra and data from reference refractometric measurements. Multiple correlation coefficient of the calibrations (R) is within the range 0,91 to 0,98 and SEC values – from 0,40 to 0,80% dry matters. Validation statistics show that the calibrations obtained in a given year can successfully predict within the same year but such correlations are not correctly predicting the SSC content in other years. Kupferman(6) pointed out that the energy is absorbed by some chemical groups like CH, OH, NH which allows to be detected and quantitatively determined various chemical compounds, e.g. chlorophyll, soluble solids, proteins etc. Such a task is not an easy one because those compounds have many structural groups in common, thus being difficult the discrimination between them. The author considers as very difficult the measurement of starch by NIR. Water being the main constituent in fruits, the discrimination of other components from it is difficult too. Slaughter, (7) studied the internal quality of peaches and nectarines non-destructively by VIS/NIR Spectroscopy. The author has given a proof that simultaneous prediction is possible of the following chemical constituents: soluble solids content ($r = 0,92$); sucrose ($r = 0,87$); sorbitol ($r = 0,88$), and chlorophyll A ($r = 0,97$). The investigations were carried out with peaches of four and nectarines of three varieties. Interactance spectra were recorded instead of those in transmittance and reflectance within the range 400-1100 nm. The optical and chemical data were pooled. Then the most informative wavelengths were determined based on data pre-processing into second derivatives. The obtained NIR models were based on the ratio of two second derivatives of optical absorption within the range 800-950 nm, or – more correctly – on the quantity $\log(1/\text{Interactance})$. As chlorophyll is concerned, it has been confirmed the well known fact about the reliable prediction of that component by spectroscopic measurements. For calibration set it has been found $r = 0,97$ for the correlation between the absorption in VIR/NIR regions and data of chemical determination of chlorophyll A with $\text{SEC} = 0,22 \text{ mg/g}$. For validation set: $r = 0,94$; $\text{SEP} = 0,23 \text{ mg/g}$.

Flesh firmness in nectarines has been investigated by Costa et al., (34). This work showed some potential for rapid grading or screening operations. Performance for firmness of flesh was better than for measurements of Brix values. Work has also been carried out investigating the use of

NIR to determine peach quality. Kawano et al.,(55,56,57) have demonstrated the possibility of NIR for determination of peaches quality as well as for on-line measurement of sugar content in mandarins and peaches.

The data in the publications of the reviewed literature are summarized in Table 1. It is clear that the test range from 600 to 1100 nm is suitable for determining various indicators of quality by the spectral transmittance of:

- apples: maturity degree; internal defects – vitreousness, mealiness, internal browning, greening-chlorophyll, bruising;
- melons: maturity degree;
- endive: internal defects;
- onions: dry matter content;
- potatoes: dry matter content;
- peaches dry matter content.

Table 1. Summarised data from referred publications

Products	Quality index	Informative wavelength, λ - nm	Measurement mode	Literature source
Onions	Dry matter	906	T	Birth et al., 1985
Potatoes	Total solids content	800-1000	T	Dull et al., 1989
Endive	Internal defects	400-1000	T	Meurens and Feth- www.inapg.inra.fr/ens_rech/siab/asteq/abstarct_3rdagm
Melons	Maturity degree	400-1000	Interactance spectra	Scotter, 1996
Avocado	Maturity (dry matter content)	1200-2400	R	Schmilovitch,1997
Apples	Internal defects – vitreousness, mealiness, internal browning	550-1150	T	Meurens and Feth- www.inapg.inra.fr/ens_rech/siab/asteq/abstarct_3rdagm
Apples	Chlorophyll	670-680	Partial light transmittance	((Herold et al., www.inapg.inra.fr/ens_rech/siab/asteq/abstarct
	Water, carbohydrates	970		
	Bruises	600-750		
Apples	Internal status	800,925,1100	R,T	ASTEQ, 1999(1 st ,2 st); Slaughter , 1995; Warner, 2000
	Maturity degree	400 – 1700	T	
	Chlorophyll	670-700, 900-960	T	
	Bruises	1200	T	
Apples	Harvest maturity by skin color, starch dry matter, firmness, titratable acidity	500-1100	R	McGlone et al., www.iop.org/EJ/journal/MST
Apples	Harvest maturity by skin color, starch dry matter, firmness, titratable acidity, pH, respiration rate	500-1100	R	Laurens and Bertrand, www.inapg.inra.fr/ens_rech/siab/asteq/abstarct_3rdagm
Apples	Harvest maturity	1100 -2198		Guilerman et al., 2001
Apples	Maturity degree	400 -1100	Partial light transmittance	Di Natale et al., 2001; Sinnaeve G, 1999
Peaches	Soluble solids content	800-1050	T	Peiris 1997
Peaches	Soluble solids content, sucrose, sorbitol	800-950	Interactance – spectra	Slaughter, 1995

* Symbols: R - reflectance, T – transmittance.

Conclusion

The literature review allows for the following conclusions to be formulated:

1. NIR Spectroscopy appears to be more and more recognized as a technique of high potential for non-destructive determination of quality and detection of defects in fruits and vegetables as well as for creating of relevant instrumentation and industrial scale devices for on-line applications;
2. The skin or peel of fruits and vegetables is a disturbing factor in the non-destructive determination of their internal quality;
3. By means of diffuse reflectance are assessed only the surface color and defects in the uppermost layer of the flesh, while the measurements in transmittance are informative about the integral quality of the fruit including that of its surface;
4. Research of NIR application related to fruit and vegetables quality appraisal is a long lasting effort requiring a great volume of spectral information in order to be accounted for the yearly changing climatic conditions and varietal peculiarities of the objects studied;
5. Apples and peaches remain being the most significant objects of implementation of NIR technologies for quality assessment.

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